Computational materials design and its application to spintronics

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What is CMD®?

- CMD®: computational materials design
  - To create/synthesize materials in computers
  - Based on first principles electronic structure calculation, i.e., quantum simulation
Design: the inverse problem of simulation
How to solve the inverse problem?

CMD® Engine

- Find Mechanisms
- Predict New Materials
- Quantum Simulation
- Integrate Mechanisms
- Analyze Physical Mechanism
- Verify Functionality

Experimental Verification
Submicron physics

Simulation/design of whole submicron structures

Quantal
Yet large scale
Real devices

Quantum simulation

Most important but
difficult scale range

Classical method
Transport properties of real device structures

An example

Parallel coupling

Antiparallel coupling

Real cpp-GMR device

~35nm
Our approach

- First-principles LDA calculation of transport properties of metals, semiconductors, alloys, layered systems and hetero structures.

- KKR Green’s function method combined with Kubo-Greenwood formula and CPA.
1. Halfmetallic AF (compensated ferrimagnets)

- When two magnetic ions exist
  - One ion more than half d, the other less than half

Ferromagnetic coupling

Superexchange works (no degeneracy)
Mechanisms

- In the case of anti-parallel coupling

Antiferromagnetic coupling

Double exchange works (degeneracy)
\((\text{ZnCrFe})\text{S}\)

Energy relative to Fermi energy (Ry)

- **Antiferro**
  - Up spin
  - Down spin

- **Ferro**

- **Spin glass**

DOS (states/Ry)

Ap — Half metallic

P — Metallic

D — Metallic
Transport properties

Anti-phase domain boundary

ferro

antiferro

Anti-phase domain boundary
Transport properties of HM AF DMS?

Anti-phase domain boundary
(Zn, Cr, Fe)S films

Parallel coupling

Anti-parallel coupling
DC conductivity of (Zn,Cr,Fe)S

1.36x10^{-3} \ \Omega\ \text{cm}

6.79x10^{-3} \ \Omega\ \text{cm}

Parallel coupling

Anti-parallel coupling

New type of HM AF: (AB)X₂

- A and B are transition metals, X is chalcogens or pnictogens,
- Choose A and B such that total valence \( d \) electrons number is 10: one being less than half-filled, another being more than half-filled: ex. (FeCr)Se₂,
- Structures: NiAs-, Zinc-blende-, chalcopyrite-, wurtzite-, NaCl-type.
NiAs-type (FeCr)Se$_2$

![DOS plots for NiAs-type (FeCr)Se$_2$](image)

- AF: half metallic
- F: metallic
- SG: metallic
antiferromagnetic disordered state $(A_{0.5}B_{0.5})X$

more than two components $(AB_{0.5}C_{0.5})X_2$

Robust half-metallicity
Magnetic moments and total energy

Total energy:
- \( E_{AF} - E_{LMD} = -17.83 \text{ mRy} \)
- \( E_F - E_{LMD} = 2.76 \text{ mRy} \)
- \( E_{\text{ordered}} - E_{\text{disordered}} = -19.1 \text{ mRy} \)
- \( E_{\text{formation}} = E_{\text{CrSe}} + E_{\text{FeSe}} - 2E_{(\text{FeCr})\text{Se}_2} = 33.5 \text{ mRy} \)

Magnetic moments:

<table>
<thead>
<tr>
<th>Materials (FeCr)Se_2</th>
<th>Local magnetic moment (( \mu_B ))</th>
<th>Total (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
<td>Fe</td>
</tr>
<tr>
<td>Ordered state</td>
<td>3.2353</td>
<td>-3.1364</td>
</tr>
<tr>
<td>Disordered state</td>
<td>3.2996</td>
<td>-3.1815</td>
</tr>
</tbody>
</table>

Stable in antiferromagnetic ordered state
Many cases exhibit HM AF

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Materials</th>
<th>$E_{\text{AF}} - E_{\text{LMD}}$ (mRy)</th>
<th>$E_{\text{FR}} - E_{\text{LMD}}$ (mRy)</th>
<th>$E_{\text{order}} - E_{\text{disorder}}$ (mRy)</th>
<th>Formation $E_A + E_B - 2E_{AB}$ (mRy)</th>
<th>$T_N$ (K)</th>
<th>MF</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAs-type structure</td>
<td>(FeCr)Se$_2$</td>
<td>-17.83</td>
<td>2.76</td>
<td>-19.10</td>
<td>33.50</td>
<td>1094</td>
<td>873</td>
<td></td>
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<tr>
<td></td>
<td>(VCo)Se$_2$</td>
<td>-7.83</td>
<td>7.69</td>
<td>-37.58</td>
<td>67.90</td>
<td>565</td>
<td>426</td>
<td></td>
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<tr>
<td></td>
<td>(FeCr)Te$_2$</td>
<td>-12.74</td>
<td>1.47</td>
<td>-8.26</td>
<td>4.89</td>
<td>612</td>
<td>521</td>
<td></td>
</tr>
<tr>
<td>Zinc-blende structure</td>
<td>(VCo)S$_2$</td>
<td>-22.14</td>
<td>3.44</td>
<td>-93.70</td>
<td>212.86</td>
<td>1101</td>
<td>1048</td>
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<tr>
<td></td>
<td>(FeCr)Se$_2$</td>
<td>-20.96</td>
<td>14.50</td>
<td>-10.90</td>
<td>33.48</td>
<td>1038</td>
<td>817</td>
<td></td>
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<tr>
<td></td>
<td>(FeCr)Te$_2$</td>
<td>-15.53</td>
<td>9.85</td>
<td>-9.20</td>
<td>15.60</td>
<td>807</td>
<td>647</td>
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<tr>
<td></td>
<td>(FeCr)Po$_2$</td>
<td>-12.59</td>
<td>6.87</td>
<td>-14.81</td>
<td>15.02</td>
<td>794</td>
<td>630</td>
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<tr>
<td>Wurtzite structure</td>
<td>(FeCr)Te$_2$</td>
<td>-10.16</td>
<td>6.98</td>
<td>-2.18</td>
<td>6.35</td>
<td>588</td>
<td>498</td>
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<tr>
<td></td>
<td>(FeCr)Se$_2$</td>
<td>-12.50</td>
<td>10.18</td>
<td>-0.90</td>
<td>13.61</td>
<td>728</td>
<td>535</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite structure</td>
<td>(VCo)S$_2$</td>
<td>-24.13</td>
<td>4.15</td>
<td>non</td>
<td>200.5</td>
<td>1159</td>
<td>1025</td>
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<tr>
<td></td>
<td>(FeCr)Se$_2$</td>
<td>-22.65</td>
<td>15.98</td>
<td>non</td>
<td>27.24</td>
<td>1235</td>
<td>1097</td>
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<tr>
<td>NaCl-type structure</td>
<td>(FeCr)S$_2$</td>
<td>-7.00</td>
<td>-4.66</td>
<td>-1.39</td>
<td>4.96</td>
<td>420</td>
<td>306</td>
<td></td>
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<tr>
<td></td>
<td>(VCo)S$_2$</td>
<td>-1.15</td>
<td>6.39</td>
<td>-29.80</td>
<td>68.09</td>
<td>94</td>
<td>67</td>
<td></td>
</tr>
</tbody>
</table>

Transition metal chalcogenides
<table>
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<tr>
<th>Crystal structure</th>
<th>Materials</th>
<th>$E_{\text{AF}} - E_{\text{LMD}}$ (mRy)</th>
<th>$E_{\text{FR}} - E_{\text{LMD}}$ (mRy)</th>
<th>$E_{\text{order}} - E_{\text{disorder}}$ (mRy)</th>
<th>Formation $E_A + E_B - 2E_{AB}$ (mRy)</th>
<th>$T_N$(K)</th>
<th>MF</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAs-type structure</td>
<td>(MnCo)N$_2$</td>
<td>-31.85</td>
<td>-8.28</td>
<td>-8.03</td>
<td>23.42</td>
<td>347</td>
<td>327</td>
<td></td>
</tr>
<tr>
<td>Zinc-blende structure</td>
<td>(MnCo)N$_2$</td>
<td>-29.34</td>
<td>9.71</td>
<td>-10.97</td>
<td>14.89</td>
<td>519</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Wurtzite structure</td>
<td>(MnCo)N$_2$</td>
<td>-24.15</td>
<td>3.51</td>
<td>-2.42</td>
<td>14.50</td>
<td>295</td>
<td>268</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite structure</td>
<td>(MnCo)N$_2$</td>
<td>-29.61</td>
<td>9.17</td>
<td>non</td>
<td>15.11</td>
<td>530</td>
<td>445</td>
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</tr>
<tr>
<td>NaCl-type structure</td>
<td>(MnCo)N$_2$</td>
<td>-26.46</td>
<td>-1.14</td>
<td>-6.87</td>
<td>15.79</td>
<td>196</td>
<td>143</td>
<td></td>
</tr>
</tbody>
</table>
Applications to GMR and TMR devices

Currently used structure

Structure using HM AF
Currently used structure:

GMR ratio 19%

Resistivity:
- 78.60 μΩcm
- 63.33 μΩcm

Layers and Materials:
- Fe_{0.85}Co_{0.15}
- Cu
- Fe_{0.85}Co_{0.15}
- Ru
- Fe_{0.85}Co_{0.15}
- Mn
Our design of new MRAM cell

GMR ratio 720%

resistivity 65.58 $\mu\Omega$cm

resistivity 536.78 $\mu\Omega$cm

$5.77\text{Å}$

$5.77\text{Å}$

$5.77\text{Å}$

$\text{Fe}_2\text{Se}_2$

$\text{Cu}_2\text{Se}_2$

$\text{ZB-}(\text{FeCr})\text{Se}_2$
Magnetic metallic layers: bcc-Cu and bcc-Fe

- 4.33 Å
- 5.77 Å
- 7.21 Å

**GMR ratio 54%**

- Resistivity: 61.89 µΩ cm
- Resistivity: 95.05 µΩ cm

ZB-(FeCr)Se$_2$
Half-metallic diluted antiferromagnetic semiconductors

GMR ratio 264%

resistivity 2.25 $\mu\Omega$cm

resistivity 8.18 $\mu\Omega$cm

GaMnAs

GaAlAs

ZB-Zn(CrFe)Se
TMR devices: nonmagnetic spacer

TMR ratio 3300%

resistivity 473 $\mu\Omega\text{cm}$

Cr$_2$S$_2$

Ca$_2$S$_2$

NiAs-(FeCr)S$_2$

resistivity 16103 $\mu\Omega\text{cm}$
2. Spin transport

- Transport properties and spin dynamics are of vital interest
  - GMR
  - spin injection / accumulation
  - current induced magnetization reversal
  - spin relaxation
  - spin-pumping / battery
  - Spin-Hall effect
- F/N/F cpp GMR structure
What is spin transport?

- Electric motive force $\rightarrow$ charge/spin current
- Spin motive force $\rightarrow$ spin/charge current

Aims: First principles calculation of
- DC conductivity
- Spin conductivity
- Spin Hall conductivity
- Inverse spin Hall conductivity
- Spin injection
- Spin accumulation
Charge and spin currents

Current operators

\[ J^c = -e \nu \]  Charge current vector

\[ J^s = (\hbar / 2) \sigma \nu \]  Spin current tensor

Correlation functions

\[ \langle J^c J^c \rangle, \quad \langle J^c J^s \rangle, \quad \langle J^s J^c \rangle, \quad \langle J^s J^s \rangle \]

where

\[ \langle O_1 O_2 \rangle^{RR} = \text{Tr} \langle O_1 G^R (E_F) O_2 G^R (E_F) \rangle \]

\[ \langle O_1 O_2 \rangle^{RA} = \text{Tr} \langle O_1 G^R (E_F) O_2 G^A (E_F) \rangle \]
Conductivities

e.g.

\[
\sigma_{zz}^{cc} = \frac{1}{2} \Re \left( \langle j_z^c j_z^c \rangle^{RR} - \langle j_z^c j_z^c \rangle^{RA} \right)
\]

\[
\sigma_{zz,zz}^{cs} = \frac{1}{2} \Re \left( \langle j_z^c j_z^s \rangle^{RR} - \langle j_z^c j_z^s \rangle^{RA} \right)
\]

\[
\sigma_{zz,z}^{sc} = \frac{1}{2} \Re \left( \langle j_z^s j_z^c \rangle^{RR} - \langle j_z^s j_z^c \rangle^{RA} \right)
\]

\[
\sigma_{zz,zz}^{ss} = \frac{1}{2} \Re \left( \langle j_z^s j_z^s \rangle^{RR} - \langle j_z^s j_z^s \rangle^{RA} \right)
\]
Spin-orbit coupling

Spin-diagonal components
scalar relativistic + $l_z \sigma_z$

Spin-off-diagonal components

$$\Delta t_{L\sigma,L'\sigma'} ; \int r^2 dr \ R_L \sigma \left( l_x \sigma_x + l_y \sigma_y \right) R_{L'\sigma'}$$
Summary

- First-principles calculation of charge and spin transport properties
- Half-metallic AF and new type of GMR
- Spin conductivity of alloy systems
- Co/CoCu/Cu hetero structure
- Quantitative discussion of spin injection/accumulation and relaxation